



LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

The Optical Properties of a Polished Uranium Surface and its Epitaxial Oxide, and the Rate of Oxide Growth Determined by Spectrophotometry

W. Siekhaus, A. Nelson

December 7, 2005

Materials Research Society Fall 2005
Boston, MA, United States
November 28, 2005 through December 2, 2005

Disclaimer

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

The Optical Properties of a Polished Uranium Surface and its Epitaxial Oxide, and the Rate of Oxide Growth Determined by Spectrophotometry

Wigbert J. Siekhaus and Art J. Nelson

Chemistry and Materials Science Directorate, Lawrence Livermore National Laboratory
Livermore, CA 94550

ABSTRACT

Wide-band reflectrometry and ellipsometry have been used to determine the optical properties n and k of freshly polished uranium and of the epitaxial oxide layer, and also the rate of oxide growth in air. Results for uranium metal as well as for epitaxial oxide are compared with single wavelength ellipsometry literature values.

INTRODUCTION

The thickness of the oxide layer grown in air on the surface of uranium is of interest to the nuclear industry. To determine it, one must know the optical constants of the underlying uranium substrate and of the oxide layer. The optical constants n (refractive index) and k (extinction coefficient) at a fixed wavelength of 546.1 nm have been evaluated in a review of preceding work to be ($n=3.1$, $k=3.9$) for uranium, and ($n=2.2$, $k=0.5$) for the oxide grown on a uranium substrate [1]. The dielectric constants (and hence n and k) of single crystal UO_2 have been measured over a wide range of energies [2,3]. However, the surface oxide grown in air on a uranium substrate is not single crystal UO_2 but shows Raman peaks of diverse oxide moieties [4] and hence the constants derived in [2,3] do not quite apply. The optical properties of the metal over a wide wavelength range can be determined accurately only by generating and holding the atomically clean sample surface in an ultra high vacuum, since uranium oxidizes rapidly. We use reflectrometry that can collect data quickly after polishing from a surface with a minimal oxide layer. We apply both reflectrometry and ellipsometry to measure properties of surface layers and to compare both techniques.

EXPERIMENTAL DETAILS

A uranium sample with a total weight impurity content of approximately 150 ppm was mechanically polished, finishing with 1 μm SiO_2 particles. The sample surface was analyzed a few seconds after polishing by a commercial reflectrometer (n&k 1700, n&k Technology Inc., Santa Clara, CA 95054) over a spectral range from 200 to 900 nm. The incident and reflected light were close to surface normal, and since data collection time was about a second, the effect of surface oxide on optical response was minimized. The same sample was analyzed subsequently by a commercial variable angle spectroscopic ellipsometer with a wide spectral range from 193 to 2200 nm (VASE, J.A. Woolam Co., Inc. Lincoln, Nebraska 68508) at 65, 70, and 75 degrees angle of incidence. The ellipsometry measurements require more time, and hence the first ellipsometry data contain a larger contribution of the surface oxide.

DISCUSSION

Optical constants of Uranium and Uranium surface oxide

Reflectance data for the metal were processed using the Cauchy dispersion relation and for the oxide by relying on Forouhi-Bloomer analysis [5,6]. Excellent agreement between measurement and analysis was found for uranium immediately after polishing and for oxide covered uranium (Fig. 1).

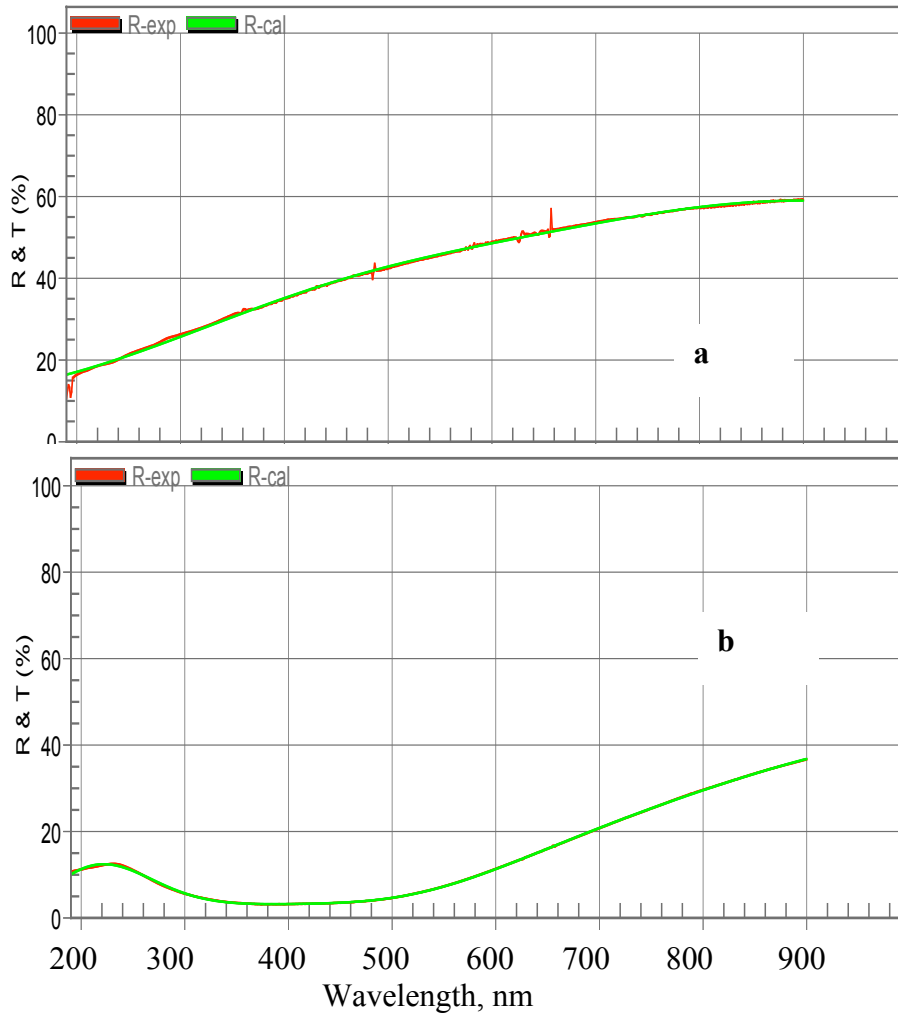


Figure 1. Experimental and calculated reflectance R as a function of wavelength of uranium surface **a)** after approximately ten seconds exposure to laboratory air, **b)** with an oxide layer approximately 28nm thick.

Bare metal reflectance at 632 nm is 0.5 (Fig. 1a). Ellipsometry data (Δ and Ψ at 65° , 70° and 75°) were analyzed by initially fitting the first measurements made after polishing to a Cauchy metal model only, secondly fitting the last measurement made on the oxidized sample to a model consisting of the uranium metal plus an oxide layer, the optical response of the oxide layer being represented by three Gaussian oscillators, thirdly refining the metal model by fitting the first

measurement made to a model consisting of metal covered with a thin oxide represented by the oscillators defined in the second step. In a fourth and final step the oxide model was refined by reanalyzing the last measurement made as consisting of a metal substrate having the optical characteristics derived in the third step and adjusting the parameters of the three Gaussian oscillators. The end result of the analysis fit Δ and Ψ of the last measurement very well, as shown in figure 2, and Δ and Ψ of the first measurement less well. Ellipsometry provides 6 data points to fit at each wavelength and is therefore much more difficult to fit exactly than reflectrometry

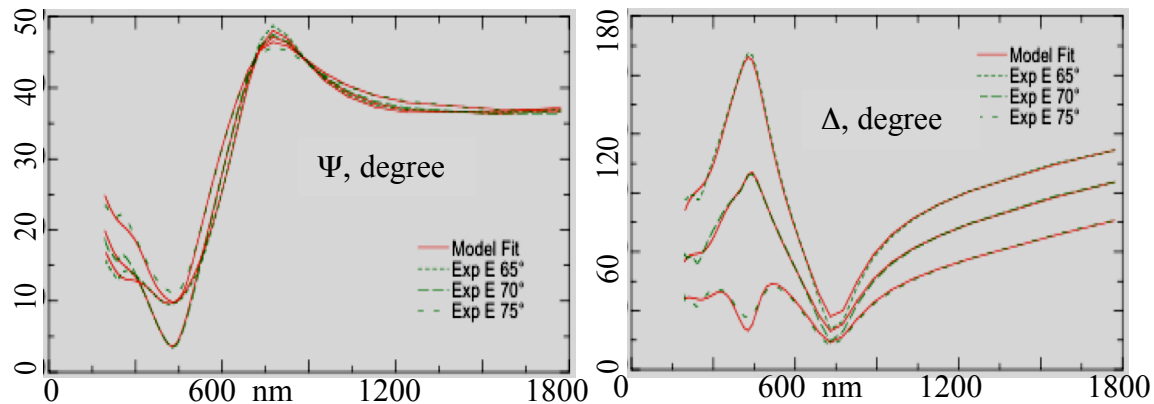


Figure 2. Ellipsometry data and fit for a 73 nm thick oxide layer on uranium.

Figure 3 shows a comparison of n and k for uranium metal deduced from reflectrometry and from ellipsometry. In addition n and k at 546 nm from [1] are plotted. Both n and k deduced from reflectrometry are substantially smaller over the whole wavelength range than n and k from ellipsometry done on this sample. The value of k reported by [1] is close to the value determined by ellipsometry in this experiment, while [1]'s value of n is higher than any value measured here by either technique over the whole wavelength range. In contrast, n and k measured by either ellipsometry or reflectrometry for the surface oxide on uranium metal, shown in figure 4, are close to each other, and close to literature values [1]. The reflectrometry values for n and k are again consistently smaller than ellipsometry's. These two analysis techniques rely on parameter fits to different models of the optical response of uranium oxide to the experimentally measured values and can both fit those well. However, ellipsometry measures a wider range of parameter and is generally accepted as the standard. The absorption coefficient at 632 nm, a typical wavelength for Raman spectroscopy, is approximately $.01 \text{ nm}^{-1}$ indicating that optical analysis of the oxide's properties can be performed on oxides with about 100nm thickness.

Oxide growth kinetics

The fitting process for both ellipsometry and reflectrometry yields the oxide thickness in addition to the optical parameters. In figure 5 reflectrometry's thickness data are shown on a double logarithmic plot as a function of time in minutes, since reflectrometry can quickly acquire data. The overall growth is well described by a diffusion controlled ($\sim \text{time}^5$) model, even though the first 10 minute's data may be better fit by an exponent greater than one half.

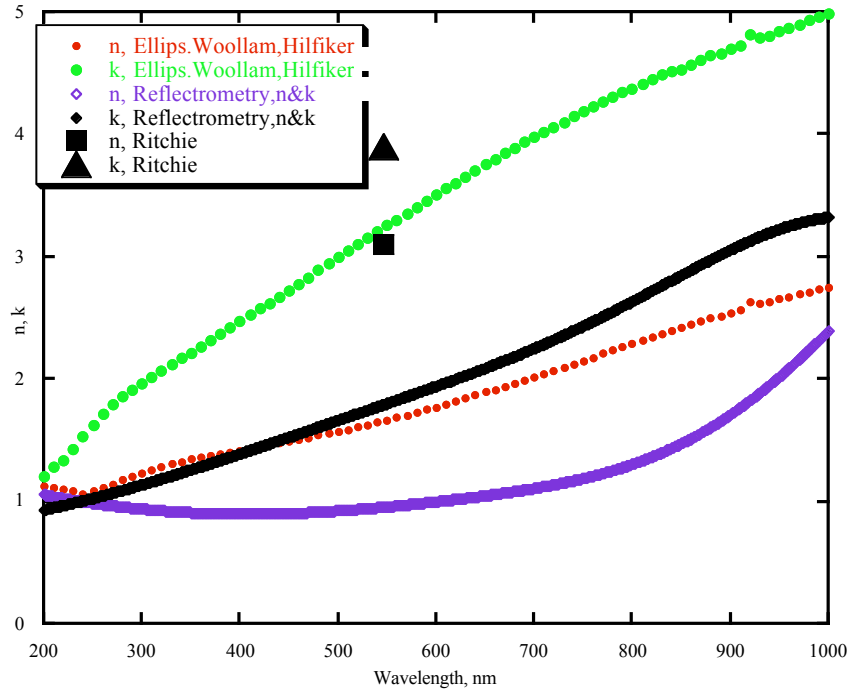


Figure 3. The optical constants n and k of bare uranium as a function of wavelength deduced from ellipsometry and reflectrometry, and literature values of n and k at 546 nm.

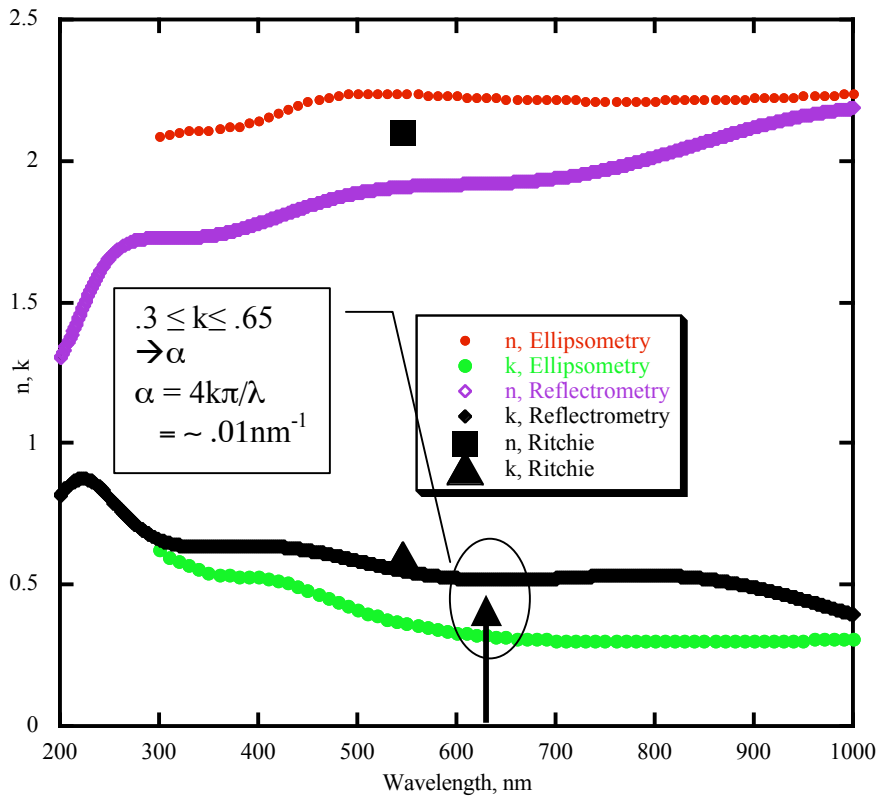


Figure 4. The optical constants n and k of surface uranium oxide as a function of wavelength deduced from ellipsometry and reflectrometry, and literature values of n and k at 546 nm.

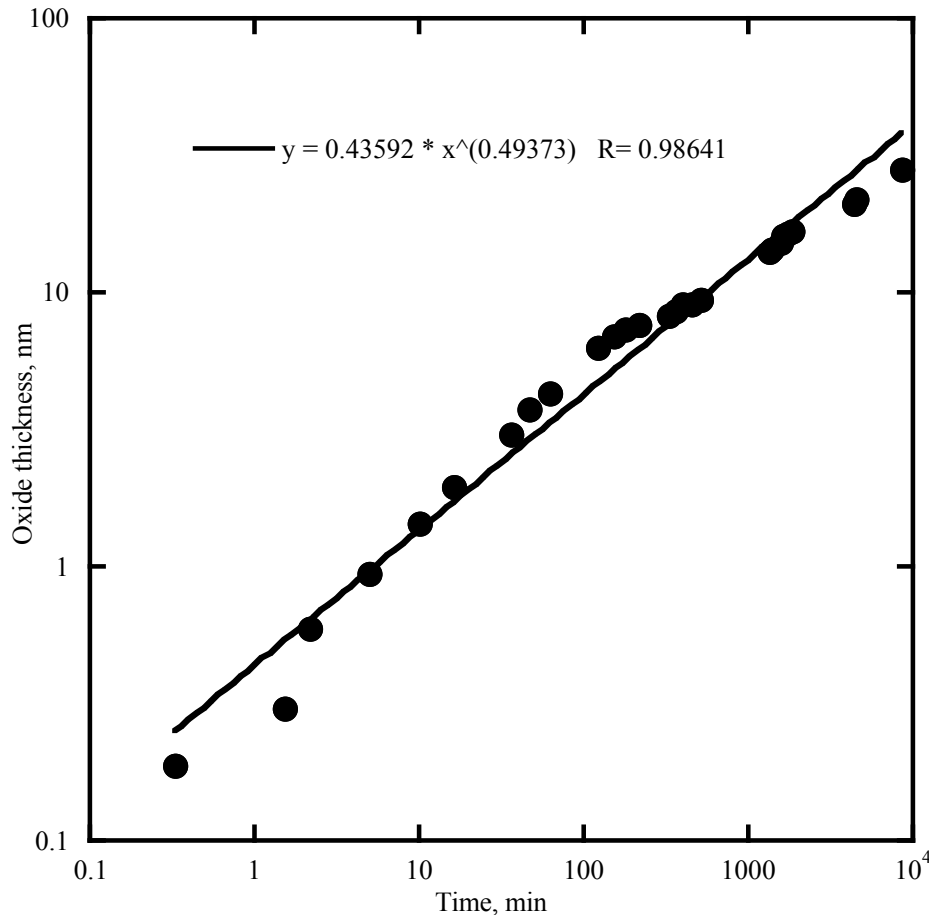


Figure 5. Uranium oxide growth kinetics determined by reflectometry.

In figure 6 the deduced thickness of both reflectometry and ellipsometry are shown on a double logarithmic plot as a function of square root of time. The first data points for ellipsometry were lost. The data from these two techniques appear to be consistent with each other. The power exponent of the fit to \sqrt{t} is, however, not one and the growth of both the reflectometry data (open squares) and the ellipsometry data (open squares with a solid square in its center) appears to decrease with time. The oxide growth is close to that determined by diffuse reflectance infrared spectroscopy, adjusted for the difference in laboratory temperature [7].

CONCLUSION

Reflectometry and ellipsometry lead to oxide growth measurements consistent with each other, even though the optical properties of the oxide determined by the two techniques differ somewhat from each other and from literature values at 546 nm, despite the fact that employ models that promise to be consistent with the Kramers-Koenig relationship. The two techniques differ strongly from each other and from literature values in the optical properties of the uranium substrate, possibly because a uranium surface polished in air have properties that differ from a sputter-cleaned or vapor-deposited surface in ultrahigh vacuum. The reflectometer used here has

a much shorter data acquisition time (seconds) and a smaller spot size (as small as 15 μm), making it possible to acquire oxide data immediately after polishing.

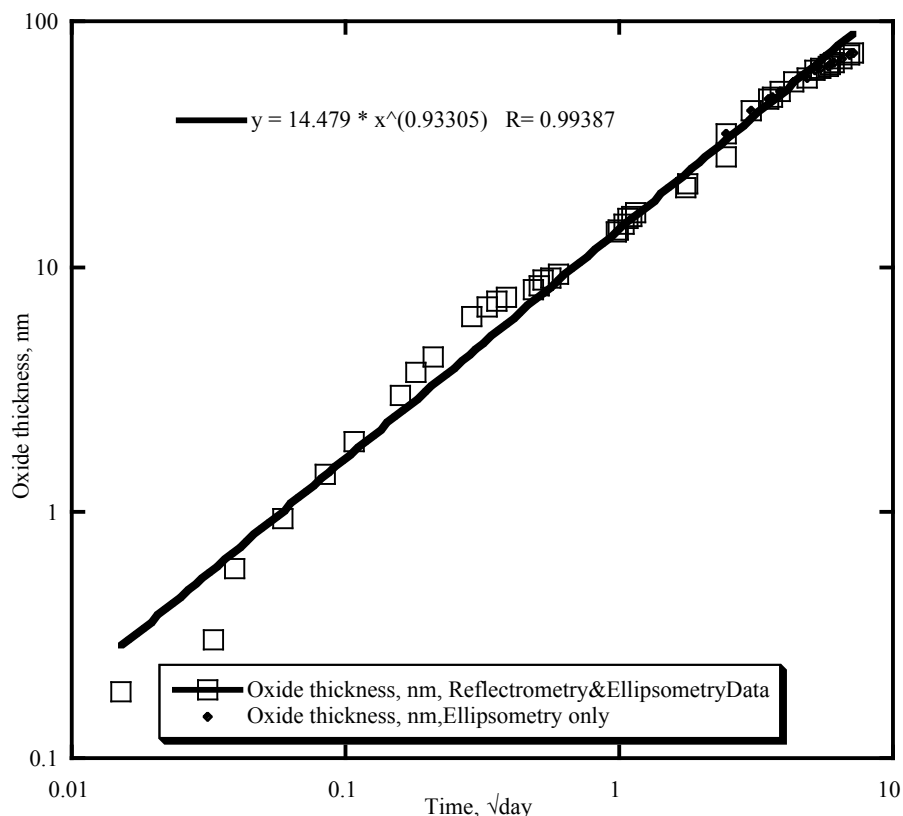


Figure 6. Uranium oxide growth data measured by both reflectrometry and ellipsometry.

ACKNOWLEDGMENTS

This work was performed under the auspices of the U. S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48. The essential help of M. Balooch of n&k Industries and of James Hilfiker and Harland Tompkins of J. A. Woollam Co. is gratefully acknowledged.

REFERENCES

1. A. G. Ritchie, *Journal of Nuclear Materials*, **120**(2-3) 143-153 (1984).
2. J. Schoenes, *Physics Reports-Review Section of Physics Letters* **63**(6) 301-336 (1980).
3. J. Schoenes, *Journal of the Chemical Society-Faraday Transactions II* **83** 1205-1213 (1987).
4. N. R. Caculitan, W. J. Siekhaus and A.J. Nelson, in *Actinides, Basic Science, Applications & Technology*, Mater. Res. Soc. Symp. Proc. Fall 2005, Boston.
5. A. R. Forouhi and I. Bloomer, *Physical Review B* **34**(10), 7018-7026 (1986).
6. A. R. Forouhi and I. Bloomer (1988), *Physical Review B* **38**(3), 1865-1874 (1987).
7. G. L. Powell, Y12, Tennessee, private communication, 2005.